ADSORPTION OF THE PESTICIDES BENTAZON, CARBOFURAN AND 2,4-DICHLOROPHENOXYACETIC ACID BY MESOPOROUS ACTIVATED CARBONS PREPARED FROM AGRICULTURE WASTE

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by

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THIS THESIS IS DEDICATE TO THE LIVING MEMORY OF MY UNCLE HAJI AHMED, MY MOTHER AND MY FATHER THOUGH DEAD BUT THEIR SOULS LIVES ON MY HEART AND MIND

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LIST OF SYMBOLS

		Unit
A	Arrhenius factor	-
$\mathrm{A_c}$	Area under breakthrough curve	-
A_i	Spectrometry absorbance	-
A_T	Constant for Temkin isotherm	L/g
B	Constant for Temkin isotherm	-
C	Solute/outlet concentration	mg/L
C_0	Initial/inlet adsorbate concentration	mg/L
C_{ad}	Difference between inlet/initial and outlet/equilibrium concentration	mg/L
C_{de}	Concentration of adsorbate desorbed	mg/L
C_e	Concentration of adsorbate at equilibrium	mg/L
C_t	Concentration of adsorbate at time, *t*	mg/L
E_a	Arrhenius activation energy of adsorption	kJ/mol
k_1	Adsorption rate constant for pseudo-first-order kinetic model	1/h
k_2	Adsorption rate constant for pseudo-second order kinetic model	g/mg h
k_{AB}	Bohart and Adams mass transfer coefficient	L/mg min
K_F	Adsorption or distribution coefficient for Freundlich isotherm	$(\mathrm{mg/g(L/mg)}^{1/n})$
K_L	Rate of adsorption for Langmuir isotherm	L/mg
K_{pi}	Adsorption rate constant for intraparticle diffusion model	$(\mathrm{mg/g\ h}^{0.5})$
k_{Th}	Thomas rate constant	mL/min mg
k_{YN}	Yoon and Nelson rate constant	min^{-1}
M	Amount of adsorbent	g
N	Total number of experiments required/data point	-
n	Constant for Freundlich isotherm	-
Q	Flow rate	mL/min
N_o	Bohart and Adams saturation concentration	mg/L
$q_{,cal}$	Calculated adsorption uptake at time, *t*	mg/g
$q_{,exp}$	Experimental adsorption uptake at time, *t*	mg/g

q_o	Thomas maximum solid-phase concentration of the solute	mg/g
q_e	Amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium	mg/g
q_{eq}	Equilibrium solute uptake in fixed-bed column	mg/g
q_m	Adsorption capacity for Langmuir isotherm	mg/g
q_t	Amount of adsorbate adsorbed per unit mass of adsorbent at time, t	mg/g
q_{total}	Total adsorbed solute quantity in fixed-bed column	mg/g
R	Universal gas constant	8.314 J/mol K
R_L	Correlation coefficient	-
S_{BET}	BET surface area	m^2/g
SSE	Sum of error squares	-
t	Time	h
t_{total}	Total flow time	min
U_o	Superficial velocity	cm/min
V	Solution volume	L
V_{eff}	Effluent volume	mL
V_{meso}	Mesopore volume	cm^3/g
V_T	Total pore volume	cm^3/g
W	Dry weight of adsorbent	g
w_{char}	Dry weight of char.	g
w_o	Dry weight of precursor	g
w_{KOH}	Dry weight of potassium hydroxide pellets	g
X	Amount of adsorbent in the column	g
x	Activated carbon preparation variable	-
Y	Predicted response	-
Z	Bed height	cm

GREEK LETTERS

ΔG^o	Changes in standard free energy	kJ/mol
ΔH^o	Changes in standard enthalpy	kJ/mol
ΔS^o	Changes in standard entropy	J/mol K
λ	Wavelength	nm
τ	Time required for 50% adsorbate for Yoon and Nelson	min

LIST OF ABBREVIATIONS

AC	Activated carbon
ANOVA	Analysis of variance
ARE	Average relative error
BS	Banana stalks
BSAC	Banana stalks activated carbon
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
CCD	Central composite design
CAC	Commercial activated carbon
DDD	Dichlorodiphenyldichloroethane
DDE	Dichlorodiphenyldichloroethylene
DDT	Dichlorodiphenyltrichloroethane
DS	Date stones
DSAC	Date stones activated carbon
2,4-D	2,4-Dichlorophenoxyacetic acid
EPA	Environmental Protection Agency
FTIR	Fourier Transform Infrared
FAO	Food and Agriculture Organization
FAC	Fiber activated carbon
GAC	Granular activated carbon
IR	Impregnation ratio
IUPAC	International Union of Pure and Applied Chemistry
MAC	Maximum acceptable concentration
MCPA	Malaysian crop life and public health association
MPOC	Malaysian palm oil council
MTZ	Mass transfer zone
PAC	Powdered activated carbon
PF	Oil palm fronds
PFAC	Palm fronds activated carbon
RSM	Response surface methodology
rpm	Rotation per minute

SEM	Scanning electron microscopy
TGA	Thermogravimetric analyzer
UK	United Kingdom
US	United States of America
VOCs	Volatile organic compounds
WHO	World health organization
2FI	Two factors interaction

PENJERAPAN RACUN PEROSAK BENTAZON, KARBOFURAN DAN ASID 2,4 –DICHLOROPHENOXYACETIC DENGAN MENGGUNAKAN KARBON TERAKTIF MESOPOROUS YANG DISEDIAKAN DARI SISA PERTANIAN

ABSTRAK

Penjerapan bentazon, karbofuran dan 2,4-diklorofenoksiasetik (2,4-D) daripada larutan akues oleh karbon terakif yang diesdiakan daripada bahan sisa pertanian (pelepah kelapa sawit, tangkai pisang dan biji kurma) telah dikaji menggunakan proses kelompok dan selanjar. Karbon teraktif meso dengan luas permukaan yang tinggi telah disediakan melalui kaedah pengaktifan fizikimia yang terdiri daripada penjerapan isi dengan kalium dioksida (KOH) dan penggasan karbon dioksida (CO_2). Pelbagai pembolehubah seperti suhu pengaktifan, tempoh pengaktifan dan nisbah jerap isi kimia (IR = w_{KOH} /w_{char}), yang mempengaruhi struktur dan prestasi karbon teraktif telah diperiksa. Keadaan optimum yang diperolehi untuk penyediaan karbon teraktif dengan menggunakan kaedah permukaan bersambut ialah 750 ^{o}C selama 3 jam dan nisbah jerap isi 3.75 untuk karbon teraktif pelepah kelapa sawit (PFAC), 740.5 ^{o}C selama 1.08 jam dan nisbah jerap isi 2.3 untuk karbon teraktif tangkai pisang (BSAC), dan 850 ^{o}C selama 2.97 jam dengan nisbah jerap isi 3.75 untuk karbon teraktif biji kurma (DSAC). Kemungkinan karbon teraktif untuk menyingkirkan racun perosak daripada larutan akues telah disiasat melalui kajjan kelompok untuk PFAC, BSAC dan DSAC dan turus untuk PFAC. Eksperimen kelompok dijalankan dengan mengkaji kesan pembolehubah-pembolehubah berikut: (i) kepekatan awal dengan julat antara 25-250 mg/L untuk bentazon dan karbofuran dan 50-300 mg/L untuk 2,4-D, (ii) masa sentuh, (iii) suhu larutan (30-50^{o}C) dan (iv) pH larutan (2-12). Garis lengkuk sesuhu perjerapan, kinetik dan termodinamik telah dikaji. Data keseimbangan penjerapan bagi semua racun perosak keatas semua karbon teraktif diperiksa dengan menggunakan mode (bentazon, karbofuran dan 2,4-D) di atas karbon teraktif (PFAC, BSAC dan DSAC) diperiksa dengan menggankea model garis lengkuk sesuhu Langmuir, Freundlich dan Temkin. Adalah didapati data untuk kesemua racun perosak sesuai diwakili oleh garis lengkuk sesuhu Langmuir dan Freundlich. Data kinetik diuji dengan model tertib-pertama-tiruan, tertib-kedua-tiruan dan model resapan intrazarah, dan diperhatikan ianya mengikuti model tertib-kedua-tiruan untuk semua sistem bagi racun perosak/karbon teraktif yang dikaji. Pembolehubah termodinamik untuk proses penyerapan, seperti entalpi piawai, entropi piawai, tenaga bebas Gibbs piawai dantenaga pengaktifan Arrhenius telah dikira. Eksperimen turus dijalankan untuk menyiasat tingkah laku perkembangan bagi bentazon, karbofuran dan 2,4-D pada PFAC. Pemerhatian terhadap pengambilan maksimum bentazon, karbofuran dan 2,4-D masing-masing didapati sebanyak 54.0, 51.1 dan 45.0 mg/g pada kepekatan awal 100, 100 dan 150 mg/L dengan kadar aliran malar 10 mL/min dan ketinggian lapisan pada 3 cm. Proses penjerapan telah disimulasikan dengan menggunakan model-model empirik (Adams-Bohart, Thomas dan Yoon-Nelson) dan pembolehubah telah dianggarkan. Pemadanan terbaik didapati dengan model Adams-Buhart. Kecekapan penjanaan semula bagi karbon teraktif yang telah digunakan adalah masing-masing sebanyak 84-96.4, 90-97 dan 82.2-90% untuk PFAC, BSAC dan DSAC, untuk tiga kitaran jerapan-penyahjerapan racun perosak menggunakan etanol sebagai pelarut. Keputusan memperlihatkan karbon teraktif yang disediakan menunjukkan prestasi yang baik untuk penyingkiran racun perosak daripada larutan berakues berbanding kerbon teraktif komersial.

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ABSTRACT

The adsorption of bentazon, carbofuran and 2,4-dichlorophenoxyacetic acid (2,4-D) from aqueous solution by activated carbons prepared from agricultural waste materials (palm oil fronds, banana stalks and date stones) was studied using batch and continuous processes. Mesoporous activated carbons with high surface areas were prepared by physiochemical activation method consisting of potassium hydroxide (KOH) impregnation and carbon dioxide (CO_2) gasification. Various parameters, such as activation temperature, activation time and chemical impregnation ratio (IR= w_{KOH} /w_{char}), which have influence on the structure and performance of the activated carbons, were examined. The optimum conditions obtained for the prepared activated carbons using response surface methodology were 750 ^{o}C at 3 h and impregnation ratio of 3.75 for palm oil fronds activated carbon (PFAC), 740.5 ^{o}C at 1.08 h and impregnation ratio of 2.3 for banana stalk activated carbon (BSAC), and 850 ^{o}C at 2.97 h with impregnation ratio of 3.75 for date stone activated carbon (DSAC). The feasibility of activated carbons to remove pesticides from aqueous solutions was investigated through batch studies using PFAC, BSAC and DSAC and in a column using PFAC. Batch experiments were carried out to study the effects of the following variables: pesticides initial concentration with the range of 25-250 mg/L for both of bentazon and carbofuran and 50-300 mg/L for 2,4-D, contact time, solution temperature (30-50 ^{o}C) and solution pH (2-12). The adsorption isotherms, kinetics and thermodynamics were studied. Adsorption equilibrium data for adsorption of all pesticides onto all activated carbons were fitted to the Langmuir, Freundlich and Temkin isotherm models. It was found that the data for all these pesticides could best be represented by the Langmuir and Freundlich isotherm models. The kinetic data were tested with pseudo-first-order, pseudo-second-order and intraparticle diffusion models, and was observed to follow the pseudo-second-order model for all the systems of pesticides/activated carbons studied. The thermodynamic parameters for the adsorption process, such as the standard enthalpy, the standard entropy, the standard Gibbs free energy and the Arrhenius activation energy of adsorption, were calculated. The column experiments were carried out to investigate the breakthrough behavior of bentazon, carbofuran and 2,4-D on PFAC. The observed maximum uptake of bentazon, carbofuran and 2,4-D was found to be 54.0, 51.1 and 45.0 mg/g at initial concentration of 100, 100 and 150 mg/L, respectively at a constant flow rate and bed height of 10 mL/min and 3 cm. The adsorption process was simulated using empirical models (Bohart-Adams, Thomas and Yoon-Nelson) and the parameters were estimated. The best fitting was obtained with Adams-Bohart model. The regeneration efficiency of spent activated carbons was found to be 84-96.4, 90-97 and 82.2-90% for PFAC, BSAC and DSAC, respectively for three cycles of pesticides adsorption-desorption using ethanol as solvent. The results of this work revealed that the prepared activated carbons demonstrated good performance for the removal of pesticides from aqueous solution compared to the commercially available type.

CHAPTER ONE
INTRODUCTION

1.0 Introduction

This chapter provides an overview of the research background. The scope covers from current scenario of pesticides usage in agriculture and how the pesticides found their way into different water sources. There is a growing need to find a more effective and economical way to address the frequent discharge of toxic chemicals, such as pesticides often used in agriculture to the environment. Various methods of pesticides removal exist, but adsorption on activated carbons derived from agricultural waste appears to be efficient and cheaper to purify polluted water. In this chapter, the problem statement and the objectives of the research, as well as the organization of the thesis are presented.

1.1 Water Pollution

Water pollution is any human-caused contamination of water that reduces its usefulness to humans and other organisms in nature. Pollutants such as pesticides, fertilizers, and hazardous chemicals often find their way into our water channels. When our water supply is contaminated, it posed a great threat to humans, animals, and plants' health unless it goes through a costly purification procedure. Water pollution can be considered in a number of ways but in simple terms it is addition of an array of unwanted contaminant elements to the water (Forster, 2003).

Pollution of surface and ground waters causes risk to human health because of the potential health hazards of their contents of inorganic and organic compounds. Pesticides are group of hazardous compounds that may pollute water due to their extensive application in agriculture. They include rodenticides, insecticides, larvacides, miticides (acaricides), mollucides, nematocides, repellants, synergists, fumigants, fungicides, algicides, herbicides, defoliants, desiccants, plant growth regulators and sterilants. Although much benefit is obtained from their uses, they have some undesirable side effects such as toxicity, carcinogenity and mutagenity (Ayranci and Hoda, 2005).

1.2 Pesticides in Agriculture Sector

Pesticides are applied to agricultural crops and amenity land as part of the normal management of those areas for best yield or general maintenance respectively (Bloomfield *et al.*, 2006). Figure 1.1 presents a summary of some of the main processes associated with the transport of pesticides through the terrestrial and aquatic environment. Pesticides concentrations in wastewater and aqueous solution are within the range of 20-400 mg/L (Barbusiński and Filipek, 2001; Abdel-Aty *et al.*, 2006).

Pesticides are indispensable in modern agriculture, but their use and/or misuse may lead to serious deterioration in water quality which could impair the use of water for purposes of crop protection, animal production or even human consumption.

The impact of agricultural chemicals on surface water and groundwater quality has become an issue of national importance. Fishes mortality, reproductive failure in birds, and acute illnesses in people have all been attributed to the ingestion of pesticides or exposure to pesticides which, usually, is the result of misapplication, careless storage, and careless disposal of unused pesticides and its containers.

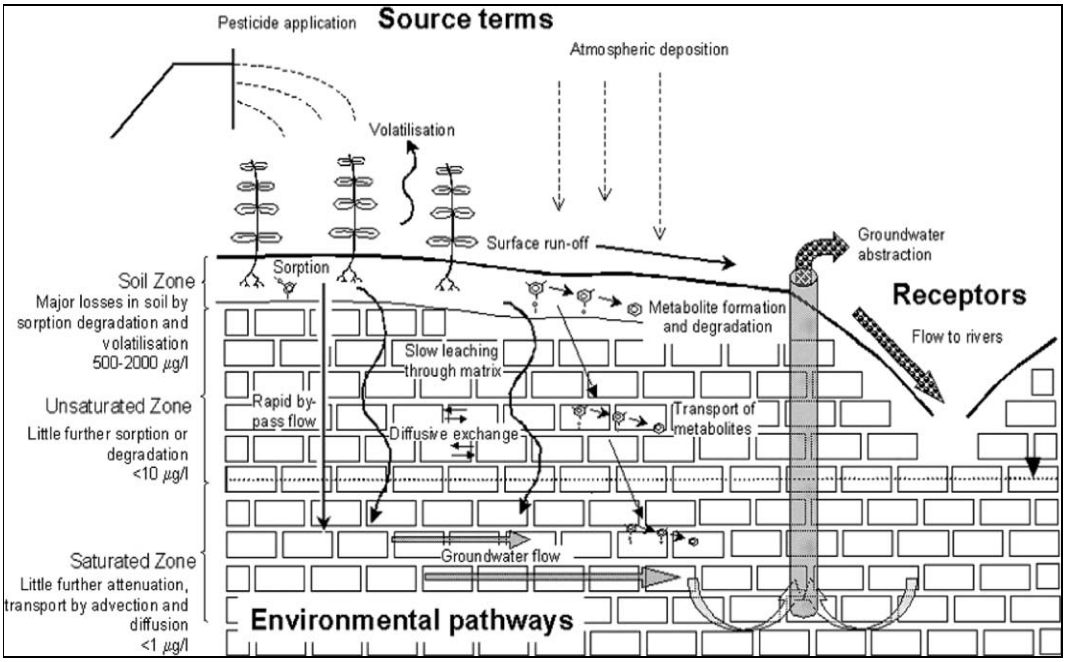

Figure 1.1: Environmental pathways for pesticides concentrations in soil (Bloomfield *et al.*, 2006).

Misuse of pesticides is not the only potential problem; groundwater contamination following normal application of pesticide has been recognized as more than just an isolated problem and hence calls for necessary attention. In addition to potential health and environmental threats, pesticide losses from fields and contamination of non-target sites (such as surface water and groundwater) represent a monetary loss to farmers (Bicki, 1989).

Malaysian Crop Life and Public Health Association (MCPA, 2005) defined pesticide as a chemical or a biological product developed and used for pests control. In agriculture, "pests" include insects, diseases, weeds and other organisms like nematodes which can have devastating effect on the quality and quantity of crops harvested for food, grain and fibre. There are a variety of pesticides to be chosen from, be it fungicides, insecticides, herbicides, rodenticides, molluscides and nematicides. In Malaysia, there is over a thousand of pesticide products registered to Department of Agriculture (Malaysian Department of Agriculture, 2006). It is estimated that about 70% of pesticides sold find application in the agricultural sector. The annual estimated crop losses in Malaysia could exceed 30% without pesticides (MCPA, 2005). On the other hand, insects, weeds, fungi, viruses, parasites, birds and rodents consume or destroy approximately 48% of the world's annual food production (Yedla and Dikshit, 2005). Crop losses could be translated into less food supply which subsequently resulted in surging of food price.

1.3 Pesticides

Pesticides are chemicals, which are commonly used in agriculture to protect crops from pest organisms including insects, plants, fungi, rodents and nematodes. They may appear as pollutants in water sources and threat to human health because of their toxicity, carcinogenicity and mutagenicity. In developed countries, drinking water quality has strict regulations regarding pesticides (Ayranci and Hoda, 2004).

Bentazon is a newly emerging herbicide used for selective control of broadleaf weeds and sedges in beans, rice, corn, peanuts, and mint. It is one of the most commonly used herbicides in agriculture and gardening. However, through leaching or run-off from agricultural lands, deposition from aerial applications and indiscriminate discharge of industrial wastewaters, bentazon has become a reckoned source of contaminant to water resources with its attendant threats to the ecosystem and environment in general; the maximum allowable concentration is 0.05 mg/L in tap water (EPA, 1998; Ayranci and Hoda, 2005).

Carbofuran is a broad spectrum systemic acaricides, insecticide and nematocide included in the general group of the carbamate derivative pesticides (Benitez *et al.*, 2002). It is widely used for the control of soil dwelling and foliar feeding insects including wireworms, white grubs, weevils, stem borers, aphids and several other insects (Kale *et al*., 2001). In Malaysia, it is used in rice fields for control of rodents and in oil palm plantations for control of rhinoceros beetles. Carbofuran is known to be more persistent than other carbamate or organophosphate insecticides (Brasel *et al*., 2007). Carbofuran is degraded in water by hydrolysis, microbial decomposition and photolysis. In the soil, it is degraded by hydrolysis, microbial action, and to a lesser extent, photodecomposition (WHO, 2004). The maximum acceptable concentration (MAC) for carbofuran in drinking water is 0.09 mg/L (SaskWater, 2008). Determining the level of carbofuran in soil or water has become increasingly important in recent years because of the widespread use of these compounds, which is due to their wide-ranging biological activity and relatively low persistence compared to organochlorine pesticides (Gavrilescu, 2005).

2,4-Dichlorophenoxyacetic acid (2,4-D) is one of the oldest herbicides used in the world. It was first developed during World War II and became famous as a component of the controversial Agent Orange used during the Vietnam War. Today, 2,4-D continues to be one of the most commonly used herbicides in the market. Because there is no longer a patent governing the manufacture and sale of 2,4-D, any company is free to produce it (Dinnage, 2007). Thus, a variety of inexpensive 2,4-D products are available from different manufacturers. 2,4-D is a selective herbicide that kills dicots (but not grasses) by mimicking the growth hormone auxin, which causes uncontrolled growth and eventually death in susceptible plants. The half-life of 2,4-D in the environment is relatively short, averaging 10 days in soils and less than ten days in water, but can be significantly longer in cold, dry soils, or where the appropriate microbial community is not present to facilitate degradation. In the environment, most formulations are degraded to the anionic form, which is water-soluble and has the potential to be highly mobile (Fu *et al*., 2009).

2,4-D is commonly used in Malaysian agriculture sector. It is used for a control of wide range of broad leaf weeds in plantation crops, such as sugar cane, oil palm, cocoa and rubber. The 2,4-D is commonly preferred because of its low cost and good selectivity. It is considered as moderately toxic and maximum allowable concentration is 0.1mg/L in drinking water (Aksu and Kabasakal, 2004). On the other hand 2,4-D is a poorly biodegradable pollutant. Consequently, it has been frequently detected in water bodies in various regions of the world. The toxicity of pesticides and their degradation products is making these chemical substances a potential hazard by contaminating the environment (El Bakouri *et al*., 2009a).

1.4 Methods of Pesticides Removal

There are several methods either independent or in conjunction that have been used for the removal of pesticides from water, such as chemical oxidation with ozone (Broseùs *et al*., 2009), photocatalytic method (Lu *et al*., 2010), combined ozone and UV irradiation (Yeasmin *et al*., 2009), Fenton degradation (Yatmaz and Uzman, 2009), biological degradation (Chen *et al*., 2009), ozonation (Rajeswari and Kanmani, 2009), membrane filtration (Liu *et al*., 2009) and adsorption (Midathana and Moholkar, 2009). Adsorption is one of the most frequently applied methods because of its efficiency, capacity and applicability on a large scale. The most commonly used adsorbent in adsorption processes is activated carbon.

Adsorption is the aggregation of solutes present in solution onto the adsorbent surface. The interaction that occurs between the surface and adsorbed species may either be physical or chemical. In the physical adsorption process, molecules are held on the carbon’s surface by weak forces known as Van Der Waals forces resulting from intermolecular attraction. The carbon and the adsorbate are thus unchanged chemically. However, in the process known as chemisorption molecules chemically react with the carbon’s surface (or an impregnate on the carbon’s surface) and are held by much stronger forces of chemical bonds.

In general terms, for adsorption to take place, it is necessary that the molecules be adsorbed onto a material having a considerable pore size. In this way the attractive forces coupled with opposite wall effect will be at a maximum and should be greater than the energy of the molecule.

1.5 Activated Carbon

Activated carbon is the most widely used adsorbent material for adsorption due to its efficiency and economic feasibility. Utilization of activated carbon can be in the form of powder, granular and fiber or cloth. Activated carbon-cloth having very high specific surface area coupled with high adsorption capacity and mechanical strength has gained increasing attention in recent years. Activated carbon is used for the removal of many pollutants from waste water by adsorption.

Recently, growing research interest in the production of carbon-based activated carbon has been focused on agricultural by-products. Low cost adsorbents derived from agricultural wastes have demonstrated outstanding capabilities for the removal of pollutants from wastewater. Therefore, low cost agricultural waste adsorbents can be viable alternatives to activated carbon for the treatment of contaminated wastewater. The use of cheap and eco-friendly adsorbents have been studied as an alternative substitution to activated carbon for the removal of dyes from wastewater (Demirbas, 2009).

The manufacturing process of activated carbon can be physical or chemical and sometimes both are employed (physiochemical method). The presence of chemicals such as potassium hydroxide during activation can impact significant effect towards porosity and surface chemistry. The availability of micropore, mesopore and macropore on activated carbon are very important and closely associated with various adsorbates molecule sizes. Microporous AC is effective to adsorb adsorbate of less than 2 nm, mesoporous AC can adsorb adsorbate of medium size, while macroporous AC uptakes adsorbate of bigger sizes, exceeding 50 nm (Sathishkumar *et al.*, 2009). Microporous activated carbon is preferred in gas phase applications because gas molecules are very small in size while mesoporous activated carbon is used widely in liquid phase applications.

Commercial activated carbon is costly because it is produced mainly from non-renewable source; therefore activated carbon produce from low-cost materials will reduce the production cost. To achieve this, the utilization of cheaper and renewable biomass which is well available such as palm oil fronds, banana stalks, date palm waste are employed.

The total area covered by palm oil (*Elaeis guianensis*) plantation in Malaysia stood at 4.3 million hectares in 2007 making. Expectedly, large and abundant quantity of palm oil fronds (PF) are naturally generated by this process, which presently are underutilized and are often buried in rows within the palm plantations (Basiron, 2007). PF is thus selected as precursors for preparation of palm oil fronds activated carbon (PFAC).

In Malaysia, banana (*Musa sapientum*) is grown in most of the states. It remains the second most important fruit crop (after durian). Most of the bananas produced are consumed locally and about 10 % are exported (Medeiros *et al.*, 2000).

Therefore an attempt was made in this work to employ banana stalk (BS) as a precursor to produce activated carbon for pesticides removal since it is abundantly available in Malaysia. Also, banana stalks activated carbon (BSAC) is cheap and renewable.

Date palm stones (*Phoenix dactylifera*) are also a low-cost, abundantly available and renewable precursor for production of activated carbon as adsorbent for the removal of pesticides from aqueous solutions. The world production of dates is about 16,696.56 million tons yearly. Iraq has long been a major producer of dates (Date palm (FAO), 2009).

1.6 Problem Statement

Increasing use of pesticides in agriculture, forestry, and domestic activities for controlling pests is polluting our water resources day by day. The leached run-off from agricultural and forest lands; deposition from aerial applications and discharge of industrial wastewater are responsible for this contamination (Gupta and Ali, 2008). Pesticides constitute a strong class of water pollutants being sometimes non biodegradable and also carcinogenic in nature. Therefore, toxicity of pesticides and their degradation products is making these chemical substances a potential hazard by contaminating our environment (Gimeno, *et al*., 2003). Presently, on a worldwide basis, intoxications attributed to pesticides have been estimated to be as high as 3 million cases of acute and severe poisoning annually, with many unreported cases and with some 220000 deaths (Kumazawa and Suzuki, 2000). This situation calls for urgent attention with acceptable solution for the removal of pesticides from water sources. This is because pesticides will continue to be used effectively for pest controls and the responsibility rest on us to find ways of avoiding many of the pesticides poisonings and contaminations that exist today.

The wide range of pesticides in use makes research extremely difficult in producing a single method for the removal of pesticides that applies universally. Several methods either independent or in conjunction with others have been used for the removal of these materials. Adsorption on activated carbon is the most widely used technology to deal with purification of water contaminated by pesticides and other hazardous chemicals. However, due to the high cost of activated carbon, its use in the field is sometimes restricted on economic considerations. In the recent times, special emphasis has been given on the preparation of activated carbons from renewable and low cost precursors.

Utilization of cheap and abundant raw materials in the production of activated carbon will to minimize the cost of its production and will as well reduces solid waste pollution. It is noteworthy to say that the selection of these cheap raw materials coupled with the proper production and application methods will both improve the efficiency of contaminant removal and reduce the cost of production of activated carbons. Therefore, it is of extreme relevance to find suitable low cost precursors that are economically attractive and at the same time able to produce activated carbons with high adsorption performance.

Agricultural biomass is considered to be very important feedstock especially in the light of two facts: they are renewable sources and low cost materials. Besides, this biomass contains high concentration of volatiles and low ash content which is ideal for creating highly porous structures within the activated carbon matrix (Dias *et al*., 2007).

In Malaysia agricultural sector produces large amount of by-products each year. Conversion of these agricultural by-products into activated carbons will turn these wastes into useful products, hence solving the waste disposal problem and second, creating useful materials from the waste. Palm oil fronds, banana stalks and date stones are used in this work as precursors to produce mesoporous activated carbons by physiochemical activation method with high surface areas and pore volumes.

From the literature survey, limited studies have been reported on the removal of bentazon (herbicide), carbofuran (insecticide) and 2,4-D (herbicide), especially using activated carbon adsorption. It is of utmost importance to remove these hazardous pollutants from aqueous solutions making precise evaluation of the adsorption performance of the activated carbons prepared for these pollutants very crucial.

1.7 Objectives of Research

The objectives of the research include:

1) To optimize the operating parameters (activation temperature, activation time and chemical impregnation ratio IR) in the preparation of mesoporous activated carbons from agriculture waste (palm oil fronds, banana stalks and date stones) for the removal of pesticides (bentazon, carbofuran and 2,4-D) from aqueous solutions.
2) To characterize the prepared activated carbons for their physical and chemical properties (surface area, pore size distribution, surface morphology, proximate content, elemental analysis and surface chemistry).

3) To study the effects of initial pesticides concentrations, contacting time, temperature and solution pH on the adsorption of bentazon, carbofuran and 2,4-D onto prepared activated carbons in batch process.
4) To study the adsorption isotherm, kinetic and thermodynamic for the pesticides onto prepared activated carbons
5) To study the fixed-bed breakthrough characteristics for adsorption of bentazon, carbofuran and 2,4-D onto palm oil fronds activated carbon (PFAC) under different conditions (pesticides inlet concentration, feed flowrates and activated carbon bed height)
6) To study the regeneration efficiency of the spent activated carbons using ethanol as a solvent.

1.8 . Organization of the Thesis

There are five chapters in this thesis which covered the work done in addition to the appendixes

Chapter one (Introduction), presents an overview on water pollutant, pesticides in agriculture sector, how these pesticides can be remove by adsorption technique using activated carbon as adsorbent which was prepared from cheap, available and renewable precursors agriculture waste.

Chapter two (Literature Review) presents a review of the literature on pesticides removal focusing on adsorption technique, activated carbons as well as activation methods for preparation of activated carbons and the optimization design for the preparation conditions. This also includes characterization of activated carbon. The adsorption isotherms, kinetics, thermodynamics and regeneration of spent activated carbons in batch system as well as the breakthrough characteristics of fixed-bed adsorption system were also studied in this chapter.

Chapter three (Materials and Methods) present the experimental work done in this research. The materials and equipments, the experimental procedures which include activated carbon preparation, experimental design, characterization and models fitting for batch and fixed-bed adsorption studies as well as activated carbon regeneration.

Chapter four presents all the acquired results and discussion on the findings. It is divided in five sections. Section one included the characterization part for all the activated carbons prepared in addition to the commercial one. Section two included the RSM software results for the prepared activated carbons (PFAC, BSAC and DSAC) and the optimum conditions. Section three included the batch (isotherm, kinetic and thermodynamic) in addition to the batch adsorber design for different solution volume per adsorbent mass ratio. Section four included the fixed-bed adsorption for the three pesticides onto PFAC and the fitting models. While in section five, the regeneration study for the spent PFAC, BSAC and DSAC using ethanol as a solvent is discussed.

Chapter five (Conclusion and Recommendations) presents the goals which obtained through this study in addition to the suggestion and recommendations points.

CHAPTER 2

LITERATURE REVIEW

2.0 Introduction

This chapter presents background information and comprehensive review of the effects of pesticides pollution in water, the chemical classification of pesticides as well as information regarding 2,4-dichlorophenoxyacetic acid, bentazon and carbofuran. The treatment technologies for pesticides removal, focusing on adsorption. This is followed by review of adsorption process with activated carbon and preparation of activated carbon from different types of precursors was discussed. In addition, mentioned in this section is the characterization of activated carbon and its applications in the removal of pesticides and other pollutants. A detailed review of literature on adsorption isotherms, kinetics, and thermodynamics in batch process were properly discussed. Finally, a brief description on breakthrough curves studies involve in the processes of regeneration for activated carbon is presented.

2.1 Pollution

The environment has since the beginning of life on earth been receiving both natural and manmade synthetic wastes materials which contains toxic substances unhealthy for sustainability. In the case of synthetic materials, the effect may be prominent even at trace concentration and may go on accumulating ultimately leading to disastrous effects on the ecological habitat even the food-chain (Yedla and Dikshit, 2005). The term "pollution," which carries with it a sense of an impurity, can be defined as a chemical or physical agent in an inappropriate location or impermissible concentration level. Pollution can be considered under the four major headings related to human activities. That is, industry, energy, transportation, and agriculture. The marked increase in human population and the industrialization of most part of the globe has brought in a whole new set of pollutants. Similarly, scientific advances based upon understanding the chemical and physical forces underlying nature have led to new processes and new products that have transformed the society and have had major positive impact on human health. Water pollution is caused by human agents by whom water is contaminated by various activities and reduces its usefulness to man and other organisms. Pollutants such as herbicides, pesticides, fertilizers, and hazardous chemicals can make their way into our water supply system. When our water supply is contaminated, it poses a threat to humans, animals, and plant health unless it goes through a costly purification procedure (EPA, 2009).

The use of pesticides in agriculture has contributed significantly to environmental pollution. Pesticides are used to control the growth of insects, weeds, and fungi, which compete with humans in the consumption of crops. Its use not only to increase crop yields and decreases grocery prices, but also controls diseases such as malaria and encephalitis. However, the spraying of crops and the runoff water from irrigation transports these harmful chemicals to the habitats of non-targeted animals. These chemicals build up in the tissues of these animals, and when consumed by man increased the potency of these pesticides and is manifested as health related problems which in some cases may result to death. Chemists have recently developed naturally occurring pesticides that are toxic only to their particular targets and are benign to birds and mammals (Coats, 1994). The most significant pesticide of the twentieth century was dichlorodiphenyltrichloroethane (DDT), which is highly effective as an insecticide but cannot be detoxified in the environment hence resulting in the death of birds, fish, and some humans (Stenersen, 2004).

2.2 Pesticides

A pesticide is any substance used for the destruction or control of pests. They include insecticides used for killing insects, herbicides used for killing weeds and other troublesome plants, fungicides for killing fungi, rodenticides for killing rodents, such as rats and mice, molluscicdes for killing snails and other mollusks and so on. Pesticides may be of the broad spectrum type which kills a wide range of organisms or the selective type which destroys one organism or few specific organisms (Magri and Haith, 2009).

Unfortunately though, scant attention is being paid to the long-term impact of chemical pesticides on our environment as well as the health hazards involved. Pesticides can be poisonous to humans as well (EPA, 2007). Pollution of surface and ground waters causes risk to environment and human health because of the potential health hazards of their contents of inorganic and organic compounds. Also, the contamination of these waters by pesticides is an arduous task that the scientists have been battling to resolve over the years. Although much benefit is obtained from the use of pesticides, they have some undesirable side effects, such as its toxicity, carcinogenic and mutagenic nature (Sarkar *et al.*, 2006; Clementia *et al.*, 2008).

Once a pesticide is introduced into the environment, whether through application, disposal or spill, it is influenced by many processes. These processes determine the pesticide persistence and movement, if any, and its ultimate impact on life in the environment which could be beneficial or detrimental. Some physical agents, for example, wind and water (surface or underground) currents can move a pesticide to its targeted area or destroy its potentially harmful residues. Sometimes they can be detrimental, leading to reduced control of a target pest, injury of non-targeted plants and animals, and environmental damage. Of particular concern today is the movement of pesticides into groundwater. Different soil and climatic factors and handling practices have been observed to promote or prevent each process. An understanding of the impact processes can help every pesticide applicator to ensure that applications are not only effective, but are also environmentally safe (Sopea *et al.*, 2009). Pesticides can be classified according to chemical class or according to their intended use. Major chemical groups that are formulated include (Saieva *et al.*, 2004; EPA, 2007; Martínez-Haro *et al.*, 2008):

- Insecticides (organophosphates, carbamates, organochlorines, pyrethroids, biorationals, and botanicals).
- Fungicides (dithiocarbamates, triazoles, MBCs, morpholines, pyrimidines, phthalamides, and inorganics).
- Herbicides (triazines, carbamates, phenyl ureas, phenoxy acids, bipyridyls, glyphosates, sulfonyl ureas, amida xylenols, and imidazole inones).
- Rodenticides (coumarins).

Above all, the main purpose of pesticide formulation is to manufacture a product which has optimum biological efficiency, convenient to use, and minimizes environmental impacts.

Pesticides are very hazardous, toxic to many forms of wildlife and persist in the aquatic environment for many years after their application (El Bakouri *et al.*, 2009a). Over the past few decades, the occurrence of organochlorine pesticides in the environment had been of great concern due to their persistence, bioaccumulation as well as their toxicological effects (Min *et al.*, 2008; El Bakouri *et al.*, 2009b).

Around 40–90% of ground and surface water contamination by pesticides is attributable to direct losses (e.g. spills during filling operations, leakages of spray equipment, spray leftovers, spills of rinsing water from cleaning of the spraying equipment) (Wilde *et al.*, 2009).

2.3 Pesticides Pollution in Water

Pesticides pollution in water may arise as a result of runoff and leaching. It is believed that only a part of the applied amount of pesticide is bioactive while the rest is distributed in the environment. Certain remaining amounts attached to the soil are leached out, migrate into groundwater or are distributed by surface runoff. A certain quantity reaches the air and can diffuse over long distances. The diagram of pesticides effect can be referred in Figure 2.1 (Cook, 2000).

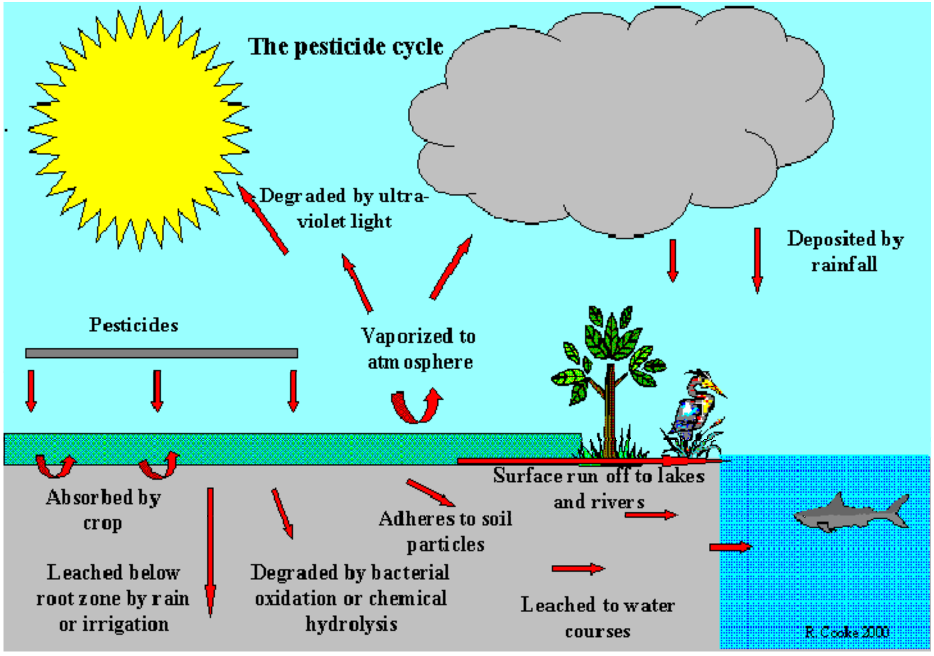

Figure 2.1: The effect of pesticides (Cook, 2000)

In Malaysia, there has been no specific local water regulation on pesticides application and content implemented by government so far. However, there is a provision for the regulation of import, manufacture and sales of pesticides which exists under the Pesticides Act 1974 (Amended in 2004). The objective of this regulation is to ensure that pesticides imported, manufactured and sold in the country are of good quality and that they will not cause adverse effects on man, food crops and the environment (Department of Agriculture, 2006).

2.4 Treatment Technologies for Pesticides Removal

The massive use of pesticides has resulted in their ubiquitous presence in the environment in the form of sub-lethal pollution, and has led to their leaching into subsurface zones and subsequent contamination of surface and ground waters. Human and animal exposure to these compounds has caused serious toxic symptoms (Abul Farah *et al.*, 2004). Pesticides are unlike heavy metals and other pollutants, pesticides are lethal to the environment even at micro level concentrations. They can also harm non-targeted organisms (Yedla and Dikshit, 2005).

Current treatment technologies for pesticides can be divided into three categories. They are chemical, physical and biological methods. Chemical treatment using advanced oxidation processes has gained interest of researchers lately due to its ability to destruct organic compounds. Biological method is still in its infancy in this area and it is still facing many challenges that needed to be overcome. On the other hand, physical treatment such as adsorption and membrane filtration has produced satisfactory results in removing pesticides from water (Alzaydien, 2009).

2.5 Adsorption

Figure 2.2 shows the mechanism of adsorption and desorption process (Henning and Degle, 1990). Adsorption is a process where a solid is used for removing a soluble substance from the polluted water. A solid surface in contact with a solution tends to accumulate or aggregate on its surface layer of solute molecules because of the imbalance that exist from the surface forces (Eckenfelder, 2000).

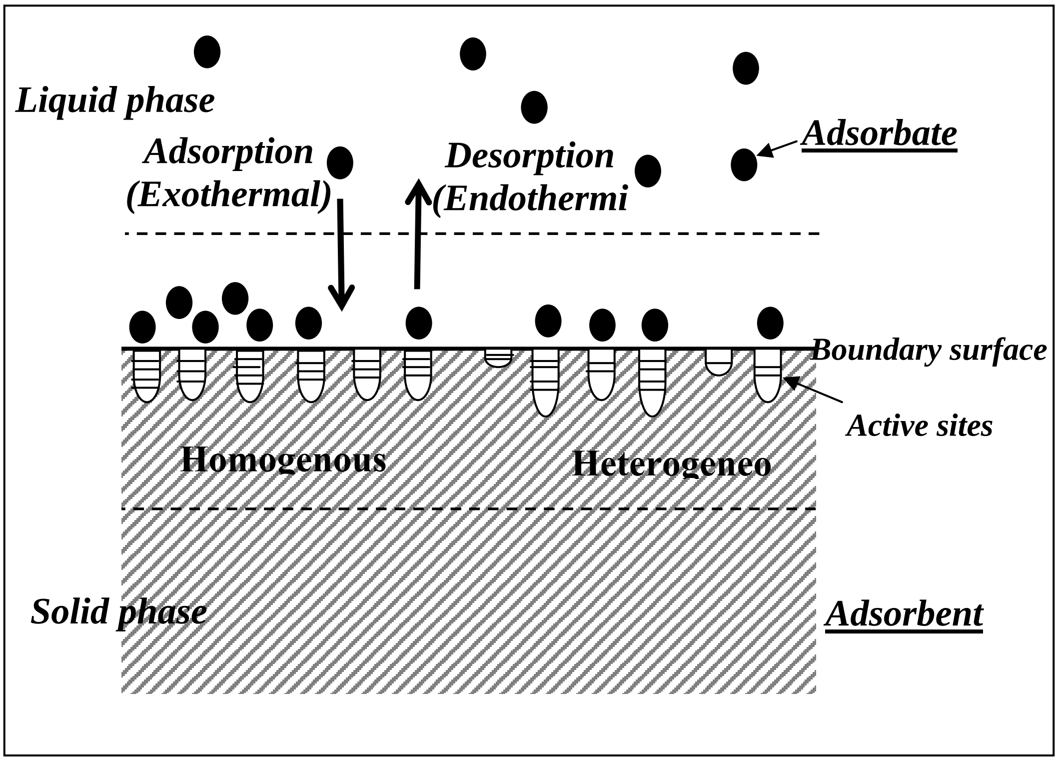

Figure 2.2: Mechanism of adsorption and desorption (Henning and Degle, 1990)

Adsorption techniques have gained popularity recently due to their efficiency in the removal of pollutants; in addition adsorption produces high quality products and is an economically feasible process (Robinson *et al.*, 2001). Adsorption is considered to be superior compared to other techniques due to its low cost, availability, simplicity of design, high efficiency, ease of operation biodegradability and ability to treat pollutants in more concentrated form (Arami *et al*., 2005). Besides, adsorption does not result in the formation of harmful substances (Crini, 2006). Adsorption is one of the most promising techniques for pesticide removal due to flexibility in design and operation (Ayar *et al.*, 2008; Tseng and Wu, 2009).

2.6 Adsorption Types

Adsorption is based on the theory that a solid surface in contact with a solution tends to accumulate or aggregate on its surface layer of solute molecules because of the unbalanced surface forces. Adsorption can result either from the universal Van der Waals interactions (physical adsorption or physisorption) or it can have the character of a chemical process (chemical adsorption or chemisorption) (Dabrowski, 2001). Generally the adsorption process involves both of chemical and physical adsorption (Ghasemi and Asadpour, 2007; Wołowicz and Hubicki, 2009; Grosman and Ortega, 2009).

2.6.1 Physical Adsorption

Physical adsorption is a readily reversible process (Mange, 2000), and it can occur when weak interparticle bonds such as Van der Waals, Hydrogen and dipole exist between the adsorbate and adsorbent. Physical adsorption results from molecular condensation in the capillaries of the solid. There is a rapid formation of an equilibrium interfacial concentration, followed by the rate of diffusion of the solute molecules within the capillary pores of the carbon particles. The rate varies reciprocally with the square of the particle diameter; it increases with increasing concentration of solute and temperature, but decreases with increasing molecular weight of the solute (Eckenfelder, 2000). An analytical representation of the measured adsorption data over the wide operating pressure and temperature swing of the system is necessary for the calculation of complete mass and energy conservation equations (Richard, *et al.*, 2009). Adsorption can occur at the interface of a condensed liquid and a gaseous phase. The increase in concentration of a dissolved substance at the interface of a condensed liquid phase is largely due to the operation of surface forces.

2.6.2 Chemical Adsorption

Chemical adsorption occurs when strong interparticle bonds are present between the adsorbate and adsorbent due to an exchange of electrons (Allen and Koumnova, 2005). Chemical adsorption on the other hand results in the formation of a monomolecular layer of the adsorbate on the surface through forces of residual valence of the surface molecules (Eckenfelder, 2000). Such interactions are often characterized by a high degree of chemical reaction or molecular configuration, specificity between the adsorbent and adsorbate that involve specific functional group reactions. It is the result of chemical interaction between the solid and the solute. The strength of the chemical bond may vary considerably and identifiable chemical compounds in the usual sense may not actually form. The adhesive force is generally greater than that found in physisorption process and the heat liberated during chemisorption is usually large in sequence of the order of heat of chemical reaction.

2.7 Activated Carbon

Activated carbon (AC) is a family of microporous materials used in a myriad of commercial applications as adsorbents for the removal of gaseous and liquid pollutants as well as many other applications. Activated carbon is the generic term used to describe a family of carbonaceous adsorbents with a highly amorphous structure and an extensively developed internal pore structure. AC is produced from a variety of carbonaceous rich materials such as wood, coal, lignin and coconut shell. The observed phenomenon for the results of adsorption on AC is largely due to its microporous surface area. This large surface area relative to the size of the actual carbon particle makes it easy to remove large amounts of impurities in a relatively small enclosed space (Gaur and Shankar, 2008).

The main distinction between gas-adsorbing and liquid-phase carbons lies in the pore size distribution. Basically, the structures of activated carbons containing pores are classified according to the International Union of Pure and Applied Chemistry (IUPAC, 1972; Sathishkumar *et al.*, 2009) into three groups are:

(i) Micropores type (pore size < 2 nm).
(ii) Mesopores type (pore size 2-50 nm).
(iii) Macropores type (pore size >50 nm).

Activated carbon includes a wide range of amorphous carbon-based materials prepared to exhibit a high degree of porosity and an extended inter-particulate surface area. The effectiveness of activated carbon as an adsorbent can be attributed to its unique properties, including large surface area, a high degree of surface reactivity, universal adsorption effect, and favorable pore size (Tseng, 2007). These qualities impart activated carbon with excellent adsorbent characteristics that made it very useful for a wide variety of processes including filtration, purification, deodorization, decolorization and separation. Activated carbons have been produced from a large number of carbonaceous raw materials such as coal, lignite, wood, coconut shell, and some agricultural waste products (Guo and Lua, 2000). Similarly, activated carbons are now frequently used in environmental processes for removing toxic gases and in wastewater as well as potable water treatments (El-Hendawy, 2005). Water treatment provides both the largest market and the main area of growth for activated carbons in fact it is known that around 80% of the world production of activated carbons is used in liquid phase applications (Dias *et al.*, 2007; Gaur and Shankar, 2008).

2.7.1 Commercial Activated Carbon for Pesticides Treatment

Activated carbon is most effective at removing organic compounds such as volatile organic compounds, pesticides and benzene. It can also remove some metals, chlorine and radon. As with any treatment system, it cannot remove all possible drinking water contaminants (Rivas *et al.*, 2003). Activated carbon has specific properties depending on the material source (precursor) and the mode of activation (Eckenfelder, 2000). In both physical and chemical activation processes, the knowledge of different variables is very important in developing the porosity of the activated carbon. The adsorption capacity of an activated carbon is related to its properties such as surface area, pore volume and pore size distribution. The development of micropores and mesopores is important as it allows the activated carbon to adsorb large amounts and various types of adsorbates either from gas or liquid streams (Wu *et al.*, 2005; Mui *et al.*, 2009).